



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

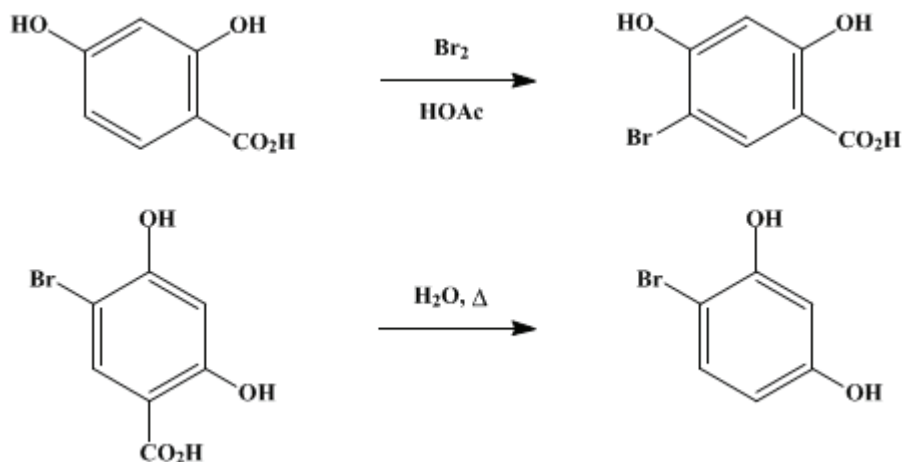
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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4-BROMORESORCINOL

[Resorcinol, 4-bromo-]



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1. Procedure

In a 1-l. flask fitted with a mechanical stirrer and a dropping funnel are placed 46.2 g. (0.3 mole) of 2,4-dihydroxybenzoic acid (β -resorcylic acid, p. 557) and 350 cc. of glacial acetic acid. After the stirrer is started the mixture is warmed until solution results (45°) and then is allowed to cool to 35° . Through the dropping funnel is added a solution of 48 g. (15 cc., 0.3 mole) of bromine in 240 cc. of glacial acetic acid with vigorous stirring over a period of about one hour. The temperature of the reaction mixture remains at $30\text{--}35^\circ$. When all the bromine is added the solution is poured into 5 l. of water, and the mixture is cooled to $0\text{--}5^\circ$ and allowed to stand for several hours. The fine, white crystals of 2,4-dihydroxy-5-bromobenzoic acid are collected on a 10-cm. Büchner funnel and washed with about 500 cc. of cold water. The crude product, after air drying at room temperature, melts at $194\text{--}200^\circ$ and weighs 55–60 g. For purification it is dissolved in 1.5 l. of boiling water, and the solution is refluxed for one hour (Note 1), filtered while hot, and cooled in an ice bath. The material which crystallizes is collected, washed with 100 cc. of cold water, and air dried. The yield of colorless 2,4-dihydroxy-5-bromobenzoic acid, melting at $206.5\text{--}208.5^\circ$ (corr.), is 40–44 g. (57–63 per cent of the theoretical amount).

Thirty grams of purified 2,4-dihydroxy-5-bromobenzoic acid is refluxed for twenty-four hours with 375 cc. of water, and the resulting solution is filtered, cooled, and extracted with a 400-cc. and a 200-cc. portion of ether. The ether is removed by evaporation, and the 4-bromoresorcinol is dried on a steam bath. The yield of product melting at $100\text{--}102^\circ$ (Note 2) is 22–22.5 g. (90–92 per cent of the theoretical amount).

2. Notes

1. The 2,4-dihydroxy-3,5-dibromobenzoic acid invariably present is in this way converted into the very soluble 2,4-dibromoresorcinol and removed. The monobromo acid is decarboxylated much more slowly.

2. Some samples were obtained with melting points ranging from 77° to 93° , but on dissolving the samples in chloroform and evaporating the solvent the values rose to $100\text{--}102^\circ$. This is not believed to be a process of purification.

3. Discussion

4-Bromoresorcinol has been prepared by the monobromination of resorcinol monobenzoate and subsequent hydrolysis;¹ from 2-bromo-5-aminophenol by the diazo reaction;² by treating resorcinol with dichlorourea and potassium bromide;³ and by the bromination of 2,4-dihydroxybenzoic acid followed by decarboxylation.⁴ The above procedure is based particularly upon the observations of Rice.⁴

References and Notes

1. Fries and Lindemann, *Ann.* **404**, 61 (1914).
2. Fries and Saftien, *Ber.* **59**, 1254 (1926).
3. Likhoshesterov, *J. Gen. Chem. (U.S.S.R.)* **3**, 172 (1933) [*C. A.* **28**, 1676 (1934)].
4. Zehenter, *Monatsh.* **2**, 480 (1881); **8**, 293 (1887); von Hemmelmayr, *ibid.* **33**, 977 (1912); **34**, 374 (1913); Rice, *J. Am. Chem. Soc.* **48**, 3125 (1926); Davis and Harrington, *ibid.* **56**, 129 (1934).

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

acetic acid (64-19-7)

ether (60-29-7)

chloroform (67-66-3)

bromine (7726-95-6)

potassium bromide (7758-02-3)

dichlorourea

resorcinol (108-46-3)

4-Bromoresorcinol,
Resorcinol, 4-bromo- (6626-15-9)

2,4-dihydroxybenzoic acid,
 β -Resorcylic acid (89-86-1)

2,4-Dihydroxy-5-bromobenzoic acid (7355-22-8)

2,4-dihydroxy-3,5-dibromobenzoic acid

2,4-dibromoresorcinol

resorcinol monobenzoate (136-36-7)

2-bromo-5-aminophenol

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